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Prof POEPPELMEIER, Kenneth R. Northwestern University, USA, 16-17 March 2005
Prof SALJE, Ekhard K.H. Cambridge University, UK, 15 September 2005

Scope of Research

Transition-metal oxides show lots of interesting and useful properties. They include ferroelectrics, ferromagnets, conductors, batteries, and so on. These materials are widely used in current electronic devices. The wide variety of their crystal structures gives rise to various electronic structures, which lead to interesting and useful physical and chemical properties. We are focusing on the fundamental physics and chemistry of these “functional oxides” and seeking new materials with new functions. We are conducting systematic studies of material synthesis based on phase equilibrium information. Precise crystal structures are analyzed by X-ray and neutron diffraction. Electronic and magnetic structures are discussed based on the results of electronic structure calculations and physical property measurements.

Research Activities (Year 2005)

Presentations

Current-Induced Electroresistive Effect in Microfabricated Perovskite Manganite thin films, Masuno A, Terashima T, Shimakawa Y, Takano M, Spring Meeting of Japan Society of Powder and Powder Metallurgy, Tokyo Japan, 1 June 2005.

A Designed New Ferromagnetic Ferroelectric $\text{Bi}_2\text{NiMnO}_6$, Azuma M, Takata K, Shimakawa Y, Takano M, Joint 20th AIRAPT-43rd EHPRG Conference on Science and Technology of High Pressure, Karlsruhe, Germany, 28 June 2005.

Search for New Functional Materials under Ultra High Pressure, Azuma M, 2005 Autumn Meeting of Physical Society of Japan, Kyoto, Japan, 20 September 2005.

New Ferromagnetic Ferroelectric Oxide with Double Perovskite Structure, Shimakawa Y, 2005 Autumn Annual Meeting of Japan Institute of Metals, Hiroshima, Japan, 29 September 2005.

New Ferromagnetic Ferroelectric $\text{Bi}_2\text{NiMnO}_6$ Compound with Double-Perovskite Structure, Shimakawa Y, Azuma M, Takata K, Hashisaka M, Kan D, Masuno A, Sakai M, Terashima T, Mibu K, Takano M, 12th US-Japan

Seminar on Dielectric and Piezoelectric Ceramics, Annapolis, U.S.A., 8 November 2005.

Thermal Stability of BaTi_2O_5 Phase, Ikeda Y, Takata K, Shimakawa Y, Asaoka Y, Takada J, Kusano Y, Fall Meeting of Japan Society of Powder and Powder Metallurgy, Shizuoka, Japan, 16 November 2005.

Grants

Shimakawa Y, Collaboratory on Electron Correlations –Toward a New Research Network between Physics and Chemistry, Grant-in-Aid for Creative Scientific Research, 1 April 2004 - 31 March 2006.

Shimakawa Y, Invention of Anomalous Quantum Materials –New Physics through Innovative Materials– Scientific Research on Priority Areas, 1 April 2005 - 31 March 2007.

Azuma, M, Search for Ferromagnetic Ferroelectrics in Lead, Bismuth-3d Transition Metal Double Perovskites with Controlled Arrangements of Elements, Natural Sciences Research Assistance, The Asahi Glass Foundation, 1 April 2005 - 31 March 2007.

Single-layer Oxychloride Superconductor $\text{Ca}_{2-x}\text{CuO}_2\text{Cl}_2$ with A-site Cation Deficiency

Superconductivity in copper oxides occurs when adequate numbers of hole or electron carriers are introduced into an antiferromagnetic insulator with CuO_2 planes. Copper oxychloride $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ shown in fig. 1(a) has a single CuO_2 plane, the same as La_2CuO_4 . Hole doping by substituting Na for Ca to make this compound superconducting was accomplished using high-pressure (HP) synthesis at 6 GPa. $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ has the highest $T_C=28$ K at $x=0.20$. The ease of sample preparation with a lightly hole-doped composition, an absence of structural changes at low temperature, an absence of structural modulation, and excellent single crystal sample cleavage are ideal for surface sensitive measurements. Investigations into this compound's electronic state using angle-resolved photoemission spectroscopy and scanning tunneling microscopy/spectroscopy are attracting great attention.

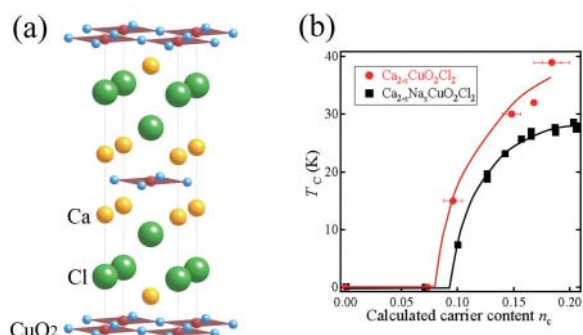


Figure 1. (a) Crystal structure of $\text{Ca}_2\text{CuO}_2\text{Cl}_2$. (b) Carrier number dependence of T_C in $\text{Ca}_{2-x}\text{CuO}_2\text{Cl}_2$ and $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$.

We have found new oxychloride superconductor $\text{Ca}_{2-x}\text{CuO}_2\text{Cl}_2$ without cation substitution by using high-pressure synthesis. The highest T_C was 38 K, 10 K higher than that of $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$. Structure analysis based on synchrotron x-ray and neutron powder diffractions revealed that the Ca deficiency was the origin of the hole carrier. This compound has two structural features as compared to $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$; fewer defects and a shorter Cu-Cl bond length. Postannealing at 773 K led to a further increase of the T_C to 43 K. This superconductor with a flat CuO_2 plane might form the basis for future discussions about the factors that determine the T_C of single-layer cuprates.

I. Yamada et al., *Phys. Rev. B*, **72**, 224503 (2005).

Pressure/Temperature/Substitution-induced Melting of A-site Charge Disproportionation in $\text{Bi}_{1-x}\text{La}_x\text{NiO}_3$ $0 \leq x \leq 0.5$

Charge ordering is a common phenomenon in mixed-valence transition-metal oxides, but it attracts much attention because of competition with fascinating metallic behavior exhibiting superconductivity or giant magnetoresistance. The competition between them has been keenly discussed as a clue for understanding the origin of such striking properties. In addition to the mixed-valence systems, several integer-valence perovskite oxides such as CaFeO_3 and ANiO_3 ($A=\text{Y, Pr, Nd} \dots$) also show a charge-ordering transition described as $2M^{n+} \rightarrow M^{(n-\delta)+} + M^{(n+\delta)+}$, which is called charge disproportionation (CD).

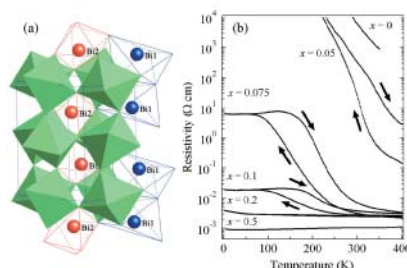


Figure 2. (a) Crystal structure of BiNiO_3 . (b) Temperature dependence of resistivity of $\text{Bi}_{1-x}\text{La}_x\text{NiO}_3$.

BiNiO_3 ($x=0$) is a triclinic perovskite with a unique valence state of $\text{Bi}^{3+}_{0.5}\text{Bi}^{5+}_{0.5}\text{Ni}^{2+}\text{O}_3$. This is the only known compound with A-site charge disproportionation. Synchrotron x-ray powder diffraction revealed that pressure ($P \sim 3$ GPa, $T=300$ K), temperature ($T \sim 340$ K, $x=0.05$), and La substitution ($x=0.075$, $T=300$ K) caused the structural change from a triclinic insulating to an orthorhombic metallic symmetry, suggesting melting of the A-site charge disproportionation. Comparing crystal structure and physical properties with the other ANiO_3 series, an electronic state of the metallic phase can be described as $\text{A}^{3+}\underline{L}$, $\text{Ni}^{2+}\underline{L}$, where a ligand-hole \underline{L} contributes to a conductivity.

S. Ishiwata et al., *Phys. Rev. B* **72**, 045104 (2005).



Figure 3. Image of “Collaboratory” on neutron diffraction studies. Real-time data sharing and video-meeting between KEK, Tsukuba and ICR, Uji.

Awards

Azuma M, Young Scientists' Prize, the Commendation for Science and Technology by the MEXT, 20 April 2005.

Ikeda Y, The L'Oréal Art & Science of Color prizes, 21 October 2005.